Density-Functional Theory of the nonlinear optical susceptibility: application to cubic semiconductors

Andrea Dal Corso

Institut Romand de Recherche Numérique en Physique des Matériaux (IRRMA), IN Ecublens,

1015 Lausanne, Switzerland.

Francesco Mauri

Department of Physics, University of California at Berkeley, Berkeley, CA 94720, USA

and Materials Science Division, Lawrence Berkeley Laboratory, Berkeley, CA 94720, USA

Angel Rubio

Departamento Física Teórica. Universidad de Valladolid. E-47011 Valladolid. Spain.

Abstract

We present a general scheme for the computation of the time dependent (TD) quadratic susceptibility ($\chi^{(2)}$) of an extended insulator obtained by applying the '$2n+1$' theorem to the action functional as defined in TD density functional theory. The resulting expression for $\chi^{(2)}$ includes self-consistent local-field effects, and is a simple function of the linear response of the system. We compute the static $\chi^{(2)}$ of nine III-V and five II-VI semiconductors using the local density approximation(LDA) obtaining good agreement with experiment. For GaP we also evaluate the TD $\chi^{(2)}$ for second harmonic generation using TD-LDA.

42.65.Ky,71.10.+x,78.20.Wc

Nonlinear optics is a growing field of research which has applications in many technical areas such as optoelectronics, laser science, optical signal processing and optical computing [1]. In these fields the description of several physical phenomena, such as optical rectification, wave-mixing, Kerr effect or multi-photons absorbtion, relies on the knowledge of the nonlinear optical (NLO) susceptibilities. Moreover nonlinear spectroscopy is a powerful tool to analyze the structural and electronic properties of extended and low dimensional systems. In the present work we give a general scheme to compute from first principles the time dependent (TD) quadratic susceptibility ($\chi^{(2)}$) of real materials within TD-density functional theory (DFT). Futhermore we show that the values of the static $\chi^{(2)}$ obtained in the local density approximation (LDA) are in good agreement with measured values for the cubic semiconductors. Our approach makes feasible the computation of $\chi^{(2)}$ in cells containing up to an hundred atoms, since it requires the same numerical effort as the computation of the total energy. This allows the evaluation of $\chi^{(2)}$ for systems of technological and scientific relevance which can not be handled by the traditional methods, such as surfaces or crystals of organic molecules.

Nowadays many first-principle calculations for the ground state properties of materials are performed within DFT. Even in its simplest form, namely in the LDA for the exchange and correlation energy this scheme gives results which, in many cases, are in surprisingly good agreement with experiments. A rigorous extension of DFT to TD phenomena has been proposed in Ref.s [2,3]. Although the available approximations for the exchange and correlation energy are less accurate in the TD domain than in the static case, this scheme is sufficiently general to allow many possible improvements in the future. Therefore TD-DFT seems to be a promising framework for the study of the NLO susceptibilities.

Standard quantum-mechanical perturbation theory can be used to compute the $\chi^{(2)}$. The straightforward application of perturbation theory leads to an expression for $\chi^{(2)}$, which diverges for an infinite solid in the static limit. However, for an insulator, these divergences have been shown to be apparent [4]. This kind of approach has been applied to compute the $\chi^{(2)}$ from first principles. The non self-consistent expression for $\chi^{(2)}$ reported in Ref. [4] has

been evaluated by Huang and Ching [5] using the DFT-LDA wavefunctions and eigenvalues. A fully self-consistent theory of the NLO susceptibility within DFT has been proposed in a series of papers by Levine and Allan [6]. Their method is feasible but algebraically very involved due to the necessity of dealing with the second order perturbation of the wavefunctions and with the apparent divergences. Their final expression is not easy to handle and its evaluation requires summations over the conduction band states, which are time consuming and difficult to converge.

In a previous paper two of us [7] have shown that it is convenient to regard the static $\chi^{(2)}$ as a third order derivative of the total energy with respect to an uniform electric field. We pointed out that this derivative can be obtained by combining a Wannier representation of the electronic wavefunctions with the '$2n+1$' theorem of perturbation theory [8,9]. We also found an equivalent expression of the static $\chi^{(2)}$ in terms of Bloch wavefunctions.

In the present letter we show that the method of Ref. [7] applies also to TD periodic perturbations and to the self-consistent TD-DFT functional. The TD $\chi^{(2)}$ can be regarded as a third order derivative of the total action. The stationary principle for the action functional [2,3], which replaces in the TD case the miminum principle for the energy functional, allows the use of the '$2n+1$' theorem. As in the static case the third order derivative depends only on the unperturbed wavefunctions and on their first order change due to the TD electric field. All the self-consistent contributions are included in the formalism in a simple way. The final expression avoids perturbation sums and does not present any apparent divergency. We apply our formalism to the computation of the the static $\chi^{(2)}$ of nine III-V and five II-VI cubic semiconductors within the LDA. For GaP we also evaluate the TD $\chi^{(2)}$ for second-harmonic generation (SHG) using TD-LDA [10].

In the Kohn and Sham (KS) formulation of DFT the ground state density $n^g(\mathbf{r})$ of a system of N interacting electrons in an external potential $V_{ext}(\mathbf{r})$ is written in terms of $N/2$ single particle wave-functions $\{\phi^g\}$. The set $\{\phi^g\}$ minimizes the KS energy functional $E[\{\phi\}]$ and the ground state energy is obtained as $E^g = E[\{\phi^g\}]$. A formalism similar to that of the static case can be introduced also in the TD domain if one restricts to Hamiltonians periodic

in time and to the evolution of the system which is steady and has the same periodicity of the Hamiltonian [11]. In TD-DFT the TD steady density $n^s(\mathbf{r}, t)$ of a system of N interacting electrons in an external TD potential $V_{ext}(\mathbf{r}, t)$, periodic in time with period T, is expressed in terms of a $N/2$ TD single particle wave-functions $\{\psi^s\}$ [2,3]. The set $\{\psi^s\}$ make stationary the KS action functional $A[\{\psi\}]$, i.e.

$$\delta A[\{\psi^s\}]/\delta\langle\psi_k(t)| = 0, \tag{1}$$

and the steady action is obtained as $A^s = A[\{\psi^s\}]$. The KS action functional $A[\{\psi\}]$ is defined as (atomic units are used throughout) :

$$A[\{\psi\}] = \int_0^T \frac{dt}{T} \left[\sum_{i=1}^{N/2} 2\langle\psi_i(t)| - \frac{1}{2}\nabla^2 - i\frac{\partial}{\partial t}|\psi_i(t)\rangle + \int d^3r V_{ext}(\mathbf{r}, t)n(\mathbf{r}, t) \right]$$
$$+ A_H[n] + A_{xc}[n].$$

Here $|\psi_i(t)\rangle = |\psi_i(t+T)\rangle$, $\langle\psi_i(t)|\psi_j(t)\rangle = \delta_{ij}$, $A_H[n] = \int_0^T dt/T \int d^3r d^3r' n(\mathbf{r}, t)n(\mathbf{r}', t)/(2|\mathbf{r} - \mathbf{r}'|)$ is the Hartree functional, $A_{xc}[n]$ is the exchange and correlation functional, and $n(\mathbf{r}, t) = \sum_{i=1}^{N/2} 2\langle\psi_i(t)|\mathbf{r}\rangle\langle\mathbf{r}|\psi_i(t)\rangle$, where the 2 factor is for spin degeneracy. At this stage no approximation for the exchange and correlation functional is made. The stationary principle in Eq. (1) yields the TD KS equations:

$$i\frac{\partial}{\partial t}|\psi_k^s(t)\rangle = [H_{KS}(t) - \epsilon_k]|\psi_k^s(t)\rangle,$$

here ϵ_k are the steady states eigenvalues, $H_{KS}(t) = -\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r}, t) + V_{Hxc}[n](\mathbf{r}, t)$ is the time dependent KS Hamiltonian, and $V_{Hxc}[n](\mathbf{r}, t) = T\delta(A_H[n] + A_{xc}[n])/\delta n(\mathbf{r}, t)$.

Now we consider a potential of the form $V_{ext}(\mathbf{r}, t, \mathbf{a}) = V_{ext}^0(\mathbf{r}) + a_1\mathbf{e}_1 \cdot \mathbf{r}\cos(\omega_1 t) + a_2\mathbf{e}_2 \cdot \mathbf{r}\cos(\omega_2 t) + a_3\mathbf{e}_3 \cdot \mathbf{r}\cos(\omega_3 t)$, where $\mathbf{e}_1$, $\mathbf{e}_2$, $\mathbf{e}_3$ are unit vectors describing the orientation of three TD uniform electric fields, $\omega_1 + \omega_2 + \omega_3 = 0$ and $\mathbf{a} = (a_1, a_2, a_3)$ describes the strength of the fields. Then the steady state wavefunctions $\{\psi^s(\mathbf{a})\}$ and action $A^s(\mathbf{a})$ depend also on $\mathbf{a}$. Note that for $\mathbf{a} = \mathbf{0}$ the potential is time independent and the action coincides with the static DFT energy. By using the Hellmann-Feynman theorem we obtain the derivative of the action with respect to the parameter a_1:

$$\frac{\partial A^s(\mathbf{a})}{\partial a_1} = \int_0^T \frac{dt}{T}\cos(\omega_1 t) \int d^3r\ \mathbf{e}_1 \cdot \mathbf{r}\ n^s(\mathbf{r}, t, \mathbf{a}) = -\mathbf{e}_1 \cdot \mathbf{P}^s(\omega_1, \mathbf{a})V,$$

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where V is the volume of the system and $\mathbf{P}^s(\omega_1, \mathbf{a})$ is the macroscopic electronic polarization per unit volume, oscillating at frequency ω_1 [12]. Then the quadratic susceptibility tensor, which is defined as $\chi^{(2)}_{\mathbf{e}_1;\mathbf{e}_2,\mathbf{e}_3}(-\omega_1;\omega_2,\omega_3) = \frac{2}{V}\frac{\partial^2 \mathbf{P}^s(\omega_1,\mathbf{0})}{\partial a_2 \partial a_3}$, is equal to:

$$\chi^{(2)}_{\mathbf{e}_1;\mathbf{e}_2,\mathbf{e}_3}(-\omega_1;\omega_2,\omega_3) = -\frac{2}{V}\frac{\partial^3 A^s(\mathbf{0})}{\partial a_1 \partial a_2 \partial a_3}.$$

The computation of the derivatives of $A^s(\mathbf{a})$ with respect to $\mathbf{a}$, can be performed by using the '$2n+1$' theorem which states that the derivatives up to order $2n+1$ of the steady action depends only on the change of the orbitals up to order n:

$$\frac{\partial^{2n+1} A^s(\mathbf{a})}{\partial \mathbf{a}^{2n+1}} = \mathcal{P}^{2n+1}\left(\frac{\partial\{\psi^s(\mathbf{a})\}}{\partial \mathbf{a}}, \cdots, \frac{\partial^n\{\psi^s(\mathbf{a})\}}{\partial \mathbf{a}^n}\right), \tag{2}$$

where $\mathcal{P}^{2n+1}$ is a polynomial of degree $2n+1$ in its arguments. Indeed, as shown in [7,8], Eq. (2) relies just on the stationary condition, Eq. (1). Therefore $\chi^{(2)}_{\mathbf{e}_1;\mathbf{e}_2,\mathbf{e}_3}(-\omega_1;\omega_2,\omega_3) = -\frac{2}{V}\mathcal{P}^3\left(\frac{\partial\{\psi^s(\mathbf{a})\}}{\partial \mathbf{a}}\right)$. The derivation of an explicit expression of $\mathcal{P}^3$ for an infinite periodic system requires a particular care because the expectation value of the $\mathbf{r}$ operator between Bloch states is ill defined. In an insulating solid this problem can be solved following Ref. [7]: first we apply the '$2n+1$' theorem in a Wannier representation where the $\mathbf{r}$ operator is well defined, then we recast the resulting expression in a Bloch representation. The final expression is:

$$\begin{aligned}
\chi^{(2)}_{\mathbf{e}_1;\mathbf{e}_2,\mathbf{e}_3}(-\omega_1;\omega_2,\omega_3) = -4\sum_{m,n}^{N/2}\sum_{\sigma=\pm}\int_{BZ}\frac{d^3k}{(2\pi)^3}\Big[&\langle u^0_{\mathbf{k},m}|\frac{\mathbf{e}_2}{2}\cdot\frac{-i\partial}{\partial\mathbf{k}}\left(|u^0_{\mathbf{k},n}\rangle\langle u^{a_1,-\sigma}_{\mathbf{k},n}|\right)|u^{a_3,\sigma}_{\mathbf{k},m}\rangle \\
&+\delta_{m,n}\langle u^{a_1,-\sigma}_{\mathbf{k},n}|V^{a_2}_{Hxc}|u^{a_3,\sigma}_{\mathbf{k},m}\rangle - \langle u^0_{\mathbf{k},m}|V^{a_2}_{Hxc}|u^0_{\mathbf{k},n}\rangle\langle u^{a_1,-\sigma}_{\mathbf{k},n}|u^{a_3,\sigma}_{\mathbf{k},m}\rangle\Big] \\
&-\frac{4}{6}\int d^3r d^3r' d^3r'' K_{xc}(\omega_2,\omega_3,\mathbf{r},\mathbf{r}',\mathbf{r}'')n^{a_1}(\mathbf{r})n^{a_2}(\mathbf{r}')n^{a_3}(\mathbf{r}'') \\
&+\Pi\{1,2,3\}.
\end{aligned} \tag{3}$$

Here $\Pi\{1,2,3\}$ indicates the sum over the 5 permutations of the indexes $1, 2, 3$, and

$$V^{a_1}_{Hxc}(\mathbf{r}) = \int d^3r'\left[\frac{1}{|\mathbf{r}-\mathbf{r}'|} + M_{xc}(\omega_1,\mathbf{r},\mathbf{r}')\right]n^{a_1}(\mathbf{r}'),$$

$$n^{a_1}(\mathbf{r}) = 2\sum_m^{N/2}\sum_{\sigma=\pm}\int_{BZ}\frac{\Omega d^3k}{(2\pi)^3}Re\left[\langle u^0_{\mathbf{k},m}|\mathbf{r}\rangle\langle\mathbf{r}|u^{a_1,\sigma}_{\mathbf{k},m}\rangle\right],$$

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$$M_{xc}(\omega_1, \mathbf{r}, \mathbf{r}') = T \int_0^T dt \frac{\delta^2 A_{xc}[n^0]}{\delta n(\mathbf{r}, 0)\delta n(\mathbf{r}', t)} e^{i\omega_1 t},$$

$$K_{xc}(\omega_2, \omega_3, \mathbf{r}, \mathbf{r}', \mathbf{r}'') = \int_0^T dt \frac{\delta M_{xc}[n^0](\omega_2, \mathbf{r}, \mathbf{r}')}{\delta n(\mathbf{r}'', t)} e^{i\omega_3 t},$$

n^0 is the unperturbed charge density, $|u^0_{\mathbf{k},m}\rangle$ is the periodic part of the unperturbed Bloch eigenstate normalized on the unit cell Ω, with eigenvalues $\epsilon^0_{\mathbf{k},m}$, and $|u^{a_1,\pm}_{\mathbf{k},m}\rangle$ are the perturbed orbitals projected on the unperturbed conduction band subspace, i.e. the solution of the linear system:

$$(\epsilon^0_{\mathbf{k},m} - H^0_{KS} \pm \omega_1)|u^{a_1,\pm}_{\mathbf{k},m}\rangle = Q_{\mathbf{k}} \left(\frac{\mathbf{e}_1 \cdot \mathbf{r}}{2} + V^{a_1}_{Hxc} \right) |u^0_{\mathbf{k},m}\rangle. \tag{4}$$

with $Q_{\mathbf{k}} = \mathbf{1} - \sum_m^{N/2} |u^0_{\mathbf{k},m}\rangle\langle u^0_{\mathbf{k},m}|$.

Note that the evaluation of Eq. (3) requires only the knowledge of unperturbed valence wavefunctions $|u^0_{\mathbf{k},m}\rangle$ and of their linear variation $|u^{a_1,\pm}_{\mathbf{k},m}\rangle$. Moreover the solution of Eq. (4) can be obtained by minimizing a suitably defined functional with a numerical effort similar to the computation of the total energy [9,13,?]. Thus our formulation makes the evaluation of $\chi^{(2)}$ in systems containing up to an hundred atoms feasible.

We have applied Eq. (3) to compute the static $\chi^{(2)}$ of nine III-V and five II-VI cubic semiconductors, evaluating the exchange and correlation energy within the LDA. We do not use any scissor operator to correct for the LDA band-gap error, contrary to what has been done in other ab-initio calculations [5,6]. Indeed the static $\chi^{(2)}$ is a ground state property, which is defined as a difference of ground state total energies and it is not related to the LDA band gap [15]. We think that improvements over LDA require a better E_{xc} functional, which could be ultra-nonlocal [16], instead of an *ad-hoc* correction of the LDA band-gap. Furthermore our purpose here is to give reference values for the static $\chi^{(2)}$ which are completely consistent within LDA.

We used norm-conserving pseudopotentials and a plane-wave kinetic energy cut-off of 24 Ry. The derivative with respect to $\mathbf{k}$ which appears in Eq. (3) has been computed by means of finite differences. We have found that the effect of d electrons is important for Ga and In atoms, and it necessary at least to use the nonlinear core corrections (NLCC) [20] to

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obtain the correct LDA values for $\chi^{(2)}$ in the compounds containing these elements [21]. For II-VI semiconductors the effect of the cation d electrons is even more important [22] and our reported values have been computed using the NLCC. For AlP, AlAs, GaP and GaAs we have also verified that our results for the $\chi^{(2)}$ reproduce the LDA values obtained in Ref. [6] if the same pseudopotentials (without NLCC) and lattice constants are used.

In Table I we report the values of the $\chi^{(2)}$ of the III-V and II-VI cubic semiconductors computed at the theoretical LDA lattice constant (a_0), also reported in the Table. On the same Table we show also the direct band-gap at the Γ point, E_Γ, and the static dielectric constant ε_∞. Known experimental values for a_0, E_Γ and ε_∞ are reported in parenthesis. Well established experimental data for $\chi^{(2)}$ do not exist since the values reported by different authors may differ by more than a factor of 2. Moreover, in some cases only data obtained at frequencies close to the absorbtion edge are available. Therefore we refer the readers to Ref.s [18,19,5] for a complete review of the experimental results. Just to give an indicative value, we show in parenthesis the experimental results from Ref. [18] which correspond to the lower frequencies. For GaP, GaAs and CdSe we have taken the values from Ref. [19] obtained after an appropriate rescaling of the experimental data. In the case of InAs we cannot compute $\chi^{(2)}$ and ε_∞ since within LDA the system is a metal. For all other compounds the computed $\chi^{(2)}$ are in the range of variation of the available experimental data [18,19,5].

As a second application we compute the TD $\chi^{(2)}$ for SHG of GaP. For this calculation we used the TD-LDA. In the TD case the use of LDA is less justified since, in general, it does not describe correctly the position of discrete excited levels and absorption edges as difference to the exact TD-DFT [3]. We note that this is a limitation of the approximation to A_{xc} used here, and *not* of Eq. (3) itself. Since LDA is not expected to perform sufficiently well in the TD domain we have used the pseudopotential without NLCC which at its theoretical lattice constant ($a_0 = 10.01$ a.u.) gives a gap ($E_\Gamma = 2.8$ eV) and thus an absorption edge, which is incidentally close to the experimental one.

In Table II we report $\chi^{(2)}(2\omega;\omega,\omega)$ computed as a function of ω in the non-absorbing

regime. The experimental measurements are taken from Ref.s [19,6].

In conclusion we have presented a consistent theory for the computation of the static and dynamic nonlinear optical susceptibilities within DFT. To this purpose we have applied for the first time the '$2n + 1$' theorem to the TD-DFT action functional. We have presented applications to cubic semiconductors. Our results show that LDA reproduces the experimental static nonlinear susceptibilities in these compounds without using any scissor operator, provided that the computations are performed at the theoretical lattice constant and NLCC are included for Ga, In, Zn and Cd atoms.

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TABLES

TABLE I. LDA nonlinear susceptibilities ($\chi^{(2)}$) of III-V and II-VI cubic semiconductors. We report also the theoretical lattice constant (a_0), the direct gap at the Γ point (E_Γ), and the dielectric constant (ε_∞). Experimental values are given in brackets. All computations are performed with 28 special **k**-points, but for InSb for which we used 60 special **k**-points.

	a_0 (a.u.)	E_Γ (eV)	ε_∞	$\chi^{(2)}$ (pm/V)
AlP	10.19 (10.33)	3.5 (3.6)	8.2 (7.5)	39 (—)
AlAs	10.56 (10.69)	2.2 (3.1)	9.3 (8.2)	64 (—)
AlSb	11.46 (11.58)	1.9 (2.3)	11.4 (11.3)	146 (98)
GaP	10.12 (10.28)	2.0 (2.9)	10.0 (9.0)	83 (74)
GaAs	10.50 (10.68)	1.0 (1.5)	12.5 (10.9)	205 (166)
GaSb	11.37 (11.49)	0.5 (0.8)	16.7 (14.4)	617 (838)
InP	10.94 (11.09)	1.0 (1.4)	10.2 (9.6)	145 (287)
InAs	11.34 (11.45)	-0.1 (0.4)	— (12.2)	— (838)
InSb	12.10 (12.23)	0.1 (0.2)	16.1 (15.7)	957 (1120)
ZnS	10.29 (10.22)	2.4 (3.8)	5.4 (5.1)	33 (61)
ZnSe	10.71 (10.71)	1.6 (2.8)	6.7 (6.3)	65 (156)
ZnTe	11.44 (11.51)	1.6 (2.4)	8.1 (7.3)	122 (184)
CdSe	11.49 (11.44)	0.8 (1.8)	6.9 (6.2)	118 (72)
CdTe	12.17 (12.24)	1.1 (1.6)	7.8 (7.1)	167 (118)

TABLE II. The frequency dependent non linear optical susceptibility for second harmonic generation of GaP, $\chi^{(2)}(2\omega; \omega, \omega)$.

$\chi^{(2)}$ pm/V	$\hbar\omega = 0.117$ eV	$\hbar\omega = 0.585$ eV	$\hbar\omega = 0.94$ eV
Theo.	68	78	103
Expt.	74 ± 4	94 ± 20	98 ± 18, 112 ± 12